

CLAIMS

1. A cell for the electrowinning of aluminium by the electrolysis of alumina dissolved in a molten fluoride-containing electrolyte, comprising one or more anodes, each having a metal-based substrate and an electrochemically-active iron oxide-based outside layer, in particular a hematite-based layer, which remains dimensionally stable by maintaining in the electrolyte a sufficient concentration of iron species, the cell operating temperature being sufficiently low so that the required concentration of iron species in the electrolyte is limited by the reduced solubility of iron species in the electrolyte at the operating temperature, which consequently limits the contamination of the product aluminium by iron to an acceptable level.

2. The cell of claim 1, wherein the iron oxide-based outside layer is either an applied layer or obtainable by oxidising the surface of the anode substrate which contains iron.

3. The cell of claim 2, wherein the anode substrate comprises a plurality of layers carrying on the outermost layer the iron oxide-based layer.

4. The cell of claim 3, wherein the anode substrate comprises an electrically conductive core layer covered with an oxygen barrier layer coated with at least one intermediate layer carrying the iron oxide-based layer.

5. The cell of claim 4, wherein the oxygen barrier layer contains chromium oxide which is covered with an intermediate layer containing copper, or copper and nickel, and/or their oxides.

6. The cell of claim 4, wherein the oxygen barrier layer contains black non-stoichiometric nickel oxide which is

covered with an intermediate layer containing copper, or copper and nickel, and/or their oxides.

✓ 7. The cell of claim 1, wherein the iron oxide-based layer is coated onto a passivatable and inert anode substrate.

8. The cell of claim 1, wherein the anode substrate comprises at least one metal, an alloy, an intermetallic compound or a cermet.)

9. The cell of claim 8, wherein the anode substrate comprises at least one of nickel, copper, cobalt, chromium, molybdenum, tantalum, iron, and their alloys or intermetallic compounds, and combinations thereof.

? 10. The cell of claim 9, wherein the anode substrate comprises an alloy consisting of 10 to 30 weight% of chromium, 55 to 90% of at least one of nickel, cobalt or iron, and 0 to 15% of aluminium, titanium, zirconium, yttrium, hafnium or niobium.

? 11. The cell of claim 9, wherein the anode substrate contains an alloy of iron and at least one alloying metal selected from nickel, cobalt, molybdenum, tantalum, niobium, titanium, zirconium, manganese and copper.

? 12. The cell of claim 11, wherein the substrate alloy comprises between 50 and 80 weight% iron and between 20 and 50 weight% nickel.

? 13. The cell of claim 12, wherein the substrate alloy comprises between 60 and 70 weight% iron and between 30 and 40 weight% nickel.

? } 14. The cell of claim 1, wherein the cell is operated with an operative temperature of the electrolyte below 910°C.

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15. The cell of claim 14, wherein the operative temperature of the electrolyte is above 700°C, preferably between 800°C and 850°C.
16. The cell of claim 1, wherein the electrolyte contains NaF and AlF₃ in a molar ratio NaF/AlF₃ comprised between 1.2 and 2.4.
17. The cell of claim 1, wherein the concentration of alumina dissolved in the electrolyte is below 10 weight%, preferably between 2 weight% and 8 weight%.
18. The cell of claim 1, comprising means for intermittently or continuously feeding iron species into the electrolyte to maintain an amount of iron species in the electrolyte preventing the dissolution of the iron oxide-based anode layer.
19. The cell of claim 18, wherein the means for feeding iron species feeds iron metal and/or an iron compound.
20. The cell of claim 19, wherein the means for feeding iron species feeds iron oxide, iron fluoride, iron oxyfluoride and/or an iron-aluminium alloy.
21. The cell of claim 18, wherein the means for feeding iron species periodically feeds the iron species together with alumina into the electrolyte.
22. The cell of claim 18, wherein the means for feeding iron species is a sacrificial electrode continuously feeding the iron species into the electrolyte.
23. The cell of claim 1, comprising at least one aluminium-wettable cathode.
24. The cell of claim 23, comprising at least one drained cathode.

25. The cell of claim 1, which is in a bipolar configuration, and wherein the anodes form the anodic side of at least one bipolar electrode and/or of a terminal anode.

26. The cell of claim 1, comprising means to improve the circulation of the electrolyte between the anodes and facing cathodes and/or means to facilitate dissolution of alumina in the electrolyte.

27. An anode which can be maintained dimensionally stable in a cell for the electrowinning of aluminium according to claim 1, having a metal-based substrate comprising at least one metal, an alloy, an intermetallic compound or a cermet, the substrate being covered with an iron oxide-based outside layer; in particular a hematite-based layer, which is electrochemically active for the oxidation of oxygen ions into molecular oxygen.

28. The anode of claim 27, wherein the iron oxide-based outside layer is either an applied layer or obtainable by oxidising the surface of the anode substrate which contains iron.

29. The anode of claim 28, wherein the iron oxide-based layer comprises a dense iron oxide outer portion, a microporous intermediate iron oxide portion and an inner portion containing iron oxide and a metal from the surface of the anode substrate.

30. The anode of claim 28, wherein the anode substrate comprises a plurality of layers carrying on the outermost layer the iron oxide-based layer.

31. The anode of claim 30, wherein the anode substrate comprises an electrically conductive core layer covered with an oxygen barrier layer coated with at least one intermediate layer carrying the iron oxide-based layer.

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32. The anode of claim 31, wherein the oxygen barrier layer contains chromium oxide which is covered with an intermediate layer containing copper, or copper and nickel, and/or their oxides.

33. The anode of claim 31, wherein the oxygen barrier layer contains black non-stoichiometric nickel oxide which is covered with an intermediate layer containing copper, or copper and nickel, and/or their oxides.

34. The anode of claim 28, wherein the iron oxide-based layer is coated onto a passivatable and inert anode substrate.

35. The anode of claims 28, wherein the anode substrate comprises at least one of nickel, copper, cobalt, chromium, molybdenum, tantalum, iron, and their alloys or intermetallic compounds, and combinations thereof.

36. The anode of claim 35, wherein the anode substrate comprises an alloy consisting of 10 to 30 weight% of chromium, 55 to 90% of at least one of nickel, cobalt or iron, and 0 to 15% of aluminium, titanium, zirconium, yttrium, hafnium or niobium.

37. The anode of claim 35, wherein the anode substrate contains an alloy of iron and at least one alloying metal selected from nickel, copper, cobalt, chromium, molybdenum, tantalum, iron, and their alloys or intermetallic compounds, and combinations thereof.

38. The anode of claim 37, wherein the alloy substrate comprises between 50 and 80 weight% iron and between 20 and 50 weight% nickel.

39. The anode of claim 38, wherein the alloy substrate comprises between 60 and 70 weight% iron and between 30 and 40 weight% nickel.

7 40. A bipolar electrode which comprises on its anodic side an anode according to claim 27.

11~ 41. A method of manufacturing an anode according to claim 27, said method comprising forming an iron oxide-based outside layer, in particular a hematite-based layer, on a metal-based anode substrate made of at least one metal, an alloy, an intermetallic compound or a cermet either by oxidising the anode surface of the substrate which contains iron, or by coating the iron oxide-based layer onto the substrate.

^ 42. The method of claim 41, wherein the iron-containing surface of the anode substrate is oxidised to form an iron oxide-based layer comprising a dense iron oxide outer portion, a microporous iron oxide portion which separates the outer portion from a two-phase inner portion, one phase containing iron oxide, the other phase containing a metal, said metal being present in the surface of the anode substrate, forming an alloy with iron.

^ 43. The method of claim 41, wherein the iron oxide-based layer is in-situ electro-deposited on the anode substrate.

^ 44. The method of claim 41, wherein the iron oxide-based layer is applied as a colloidal and/or polymeric slurry, and dried and/or heat treated.

7 45. The method of claim 44, wherein the colloidal and/or polymeric slurry comprises at least one of alumina, ceria, lithia, magnesia, silica, thoria, yttria, zirconia, tin oxide and zinc oxide.

Yannula 46. The method of claim 41, wherein the iron oxide-based layer is formed by plasma spraying iron oxide or iron onto the anode substrate followed by an oxidation treatment.

^ 47. The method of claim 41, wherein the iron oxide-based layer is formed, or consolidated, by heat treating an

7. anode substrate, the surface of which contains iron and/or iron oxide, in an oxidising gas at a temperature which is at least 50°C above the operative temperature of the cell in which the anode is to be inserted for a period of at least 1 hour.

8. 48. The method of claim 45, wherein the anode substrate is heat treated at a temperature of 950°C to 1300°C, preferably 1050°C to 1200°C.

8. 49. The method of claim 46, wherein the anode substrate is heat treated for a period of 2 to 10 hours at a temperature above 1150°C or for a period of at least 6 hours when the temperature is below 1050°C.

8. 50. The method of claim 46, wherein the anode substrate is heat treated in air or in oxygen.

8. 51. The method of claim 41, wherein the iron oxide-based layer is formed on an anode substrate comprising a plurality of layers.

8. 52. The method of claim 51, wherein the anode substrate is made by forming on a core layer an oxygen barrier layer which is coated with at least one intermediate layer and the iron oxide-based outside layer, said oxygen barrier layer being formed before or after application of the intermediate layer(s).

8. 53. The method of claim 52, wherein the oxygen barrier layer is formed by applying a coating onto the core layer before application of the intermediate layer(s) or by surface oxidation of the core layer before or after application of the intermediate layer(s).

8. 54. The method of claim 53, wherein the oxygen barrier layer and/or the intermediate layer is/are formed by slurry application of a precursor.

55. The method of claim 53, wherein the oxygen barrier layer and/or the intermediate layer is/are formed by plasma spraying oxides thereof, or by plasma spraying metals and forming the oxides by heat treatment.

56. The method of claim 52, wherein the oxygen barrier layer contains chromium oxide which is covered with an intermediate layer containing copper, or copper and nickel, and/or their oxides.

57. The method of claim 52, wherein the oxygen barrier layer contains black non-stoichiometric nickel oxide which is covered with an intermediate layer containing copper, or copper and nickel, and/or their oxides.

58. The method of claim 41, wherein the iron oxide-based layer is coated onto a passivatable and inert anode substrate.

59. The method of claims 41, wherein the anode substrate comprises at least one of nickel, copper, cobalt, chromium, molybdenum, tantalum, iron, and their alloys or intermetallic compounds, and combinations thereof.

60. The method of claim 59, wherein the anode substrate comprises an alloy consisting of 10 to 30 weight% of chromium, 55 to 90% of at least one of nickel, cobalt or iron, and 0 to 15% of aluminium, titanium, zirconium, yttrium, hafnium or niobium.

61. The method of claim 59, wherein the anode substrate contains an alloy of iron and at least one alloying metal selected from nickel, copper, cobalt, chromium, molybdenum, tantalum, iron, and their alloys or intermetallic compounds, and combinations thereof.

62. The method of claim 59, wherein the substrate alloy comprises between 50 and 80 weight% iron and between 20 and 50 weight% nickel.

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63. The method of claim 59, wherein the substrate alloy comprises between 60 and 70 weight% iron and between 30 and 40 weight% nickel.

64. The method of claim 41, wherein the anode is joined directly or through one or more intermediate layers to a cathode layer to form a bipolar electrode.

65. The method of claim 42, for reconditioning an anode according to claim 31 whose iron oxide-based layer is damaged, the method comprising clearing at least the damaged parts of the iron oxide-based layer from the anode substrate and then reconstituting at least the iron oxide-based layer.

66. A method of producing aluminium in a cell according to claim 1, the cell comprising an anode having a metal-based anode substrate and an iron oxide-based outside layer, in particular a hematite-based layer, which is electrochemically active for the oxidation of oxygen ions into molecular oxygen, said method comprising keeping the anode dimensionally stable during electrolysis by maintaining a sufficient concentration of iron species in the electrolyte, and operating the cell at a sufficiently low temperature so that the required concentration of iron species in the electrolyte is limited by the reduced solubility of iron species in the electrolyte at the operating temperature, which consequently limits the contamination of the product aluminium by iron to an acceptable level.

67. The method of claim 66, wherein the cell is operated with an operative temperature of the electrolyte below 910°C.

68. The method of claim 67, wherein the cell is operated at an electrolyte temperature above 700°C, preferably between 800°C and 850°C.

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79. The method of claim 66, wherein the cell is operated with an electrolyte containing NaF and AlF₃ in a molar ratio NaF/AlF₃ comprised between 1.2 and 2.4.

80. The method of claim 66, wherein the amount of dissolved alumina contained in the electrolyte is maintained is below 10 weight%, preferably between 2 weight% and 8 weight%.

81. The method of claim 66, wherein the amount of dissolved iron preventing dissolution of the iron oxide-based anode layer is such that the product aluminium is contaminated by no more than 2000 ppm iron, preferably by no more than 1000 ppm iron, and even more preferably by no more than 500 ppm iron.

82. The method of claim 66, wherein iron species are intermittently or continuously fed into the electrolyte to maintain the amount of iron species in the electrolyte which prevents at the operating temperature the dissolution of the anode iron oxide-based layer.

83. The method of claim 72, wherein the iron species are fed in the form of iron metal and/or an iron compound.

84. The method of claim 73, wherein the iron species are fed into the electrolyte in the form of iron oxide, iron fluoride, iron oxyfluoride and/or an iron-aluminium alloy.

85. The method of claim 74, wherein the iron species are periodically fed into the electrolyte together with alumina.

86. The method of claim 72, wherein a sacrificial electrode continuously feeds the iron species into the electrolyte.

87. The method of claim 66, for producing aluminium on an aluminium-wettable cathode.

78. The method of claim 76, wherein the produced aluminium continuously drains from said cathode.

79. The method of claim 66, for producing aluminium in a bipolar cell according to claim 27, comprising passing an electric current from the surface of the terminal cathode to the surface of the terminal anode as ionic current in the electrolyte and as electronic current through the bipolar electrodes, thereby electrolysing the alumina dissolved in the electrolyte to produce aluminium on each cathode surface and oxygen on each anode surface.

80. The method of claim 66, comprising circulating the electrolyte between the anodes and facing cathodes thereby improving dissolution of alumina into the electrolyte and/or improving the supply of dissolved alumina under the active surfaces of the anodes.

81. A cell component which can be maintained dimensionally stable in a cell for the electrowinning of aluminium according to claim 1, having an iron oxide-based outside layer, in particular a hematite-based layer, which is electrochemically active for the oxidation of oxygen ions into molecular oxygen.

82. The cell component of claim 81, wherein the hematite-based layer covers a metal-based substrate comprising at least one metal, an alloy, an intermetallic compound or a cermet.

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